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<b>(21) International Application Number:</b> PCT/US91/00835 <b>(22) International Filing Date:</b> 7 February 1991 (07.02.91)  <b>(30) Priority data:</b> 477,791 9 February 1990 (09.02.90) US  <b>(60) Parent Application or Grant</b> <b>(63) Related by Continuation</b> US 477,791 (CIP) Filed on 9 February 1990 (09.02.90)  <b>(71) Applicant (for all designated States except US):</b> EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036-0710 (US).	<b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> TURNER, Howard, William [US/US]; 303 Elder Glen, Webster, TX 77598 (US). HLATKY, Gregory, George [US/US]; 1114 Indi- an Autumn, Houston, TX 77062 (US).  <b>(74) Agents:</b> KURTZMAN, Myron, B. et al.; Exxon Chemical Company, P.O. Box 5200, Baytown, TX 77522-5200 (US).  <b>(81) Designated States:</b> AT (European patent), AU, BE (Euro- pean patent), BR, CA, CH (European patent), DE (Eu- ropean patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European pa- tent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent), SU, US.  <b>Published</b> <i>With international search report.</i>	
<b>(54) Title:</b> BLOCK COPOLYMERS FROM IONIC CATALYSTS  <b>(57) Abstract</b>  A process for the production of block copolymers of ethylene and an $\alpha$ -olefin such as propylene by using an ionic catalyst system including a metallocene component and a component having a cation capable of donating a proton and a compatible non-coordinating anion. Novel block copolymers are produced.		

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## BLOCK COPOLYMERS FROM IONIC CATALYSTS

SPECIFICATIONCross-Reference to Related Applications

1 This application is a Continuation-in-Part of U.S. Patent  
2 Application No. 477,791 filed February 9, 1990. U.S. Patent Application  
3 No. 477,791 is in turn a Continuation-in-Part of copending U.S. Patent  
4 Application Nos. 133,052 filed December 21, 1987 and 133,480 filed  
5 December 22, 1987. Copending U.S. Patent Application No. 133,052 is in  
6 turn a Continuation-in-Part of U.S. Patent Application No. 011,471 filed  
7 January 30, 1987. Copending U.S. Patent Application No. 133,480 is in  
8 turn a Continuation-in-Part of U.S. Patent Application No. 008,800 filed  
9 January 30, 1987.

FIELD OF THE INVENTION

10 This invention relates to a method for preparing block and  
11 tapered copolymers by polymerizing ethylene and other olefins in the  
12 presence of a catalyst which is a reaction product of a metallocene  
13 component with second component which comprises a cation capable of  
14 donating a proton and a compatible non-coordinating anion. More  
15 particularly, this invention relates to a process for the production  
16 of multiblock and tapered copolymers of ethylenically unsaturated  
17 monomers. The invention also related to the multiblock and tapered  
18 copolymers produced.

BACKGROUND OF THE INVENTION

19 Block copolymers are well known. They have been used  
20 commercially as components in adhesives, as melt processable rubbers,

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1 impact resistant thermoplastics, and as compatibilizers, or  
2 "surfactants", for emulsifying polymer-polymer blends.

3       There has been widespread interest in polymer blends and  
4 alloys. Unfortunately, most homopolymer pairs are immiscible with one  
5 another and give rise to low strength materials due to the lack of  
6 interfacial adhesion between the separate phases. A block copolymer  
7 is created when two or more polymeric segments, or blocks, of  
8 different chemical composition are covalently bonded in an end-to-end  
9 fashion. Block copolymers have certain advantages over blends.  
10 Firstly, the segments are covalently bonded to each other, thereby  
11 eliminating the interface problem. Secondly, block copolymers can be  
12 used to strengthen blends of immiscible polymers by serving as  
13 "emulsifiers," which encourage physical connections between the phase,  
14 and thus improve the interfacial adhesion and load transferring  
15 capability of the components.

16       While a wide variety of block copolymer architectures are  
17 possible, most block copolymers of interest involve the covalent  
18 bonding of hard plastic segments which are crystalline or glassy, to  
19 elastomeric blocks forming thermoplastic elastomers. Other block  
20 copolymers, such as rubber-rubber, glass-glass, and glass-crystalline  
21 block copolymers are also possible and may have commercial  
22 importance. Two common types of block copolymer structures are the  
23 diblock and triblock forms. However, multiblock copolymers, in which  
24 more than three segments are bonded together, are also desirable.

25       Triblock and multiblock copolymers have the unique ability of  
26 behaving as thermoplastic elastomers, combining thermoplasticity with  
27 rubber-like behavior. The key requirements for achieving  
28 thermoplastic elastomeric behavior is the ability to develop a  
29 two-phase physical network. Such a system is composed of a minor  
30 fraction of hard block, having a glass transition temperature ( $T_g$ ) or  
31 melting temperature ( $T_m$ ) above room temperature, and a major fraction  
32 of a soft block, having a  $T_g$  below room temperature. The hard blocks  
33 associate to form small morphological domains that serve as physical  
34 crosslinking and reinforcement sites. These states are thermally  
35 reversible making it possible to process the polymer as a melt at

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1 temperatures above the Tg or Tm of the hard block.

2 Block copolymers are similar to, yet distinct from, tapered  
3 polymers. In a tapered copolymer the composition of comonomer is  
4 gradually varied from one end of the polymer to the other. Tapered  
5 copolymers are commercially used as viscosity modifiers, oil  
6 additives, thermoplastic elastomers, and impact-resistant plastics.

7 Much work has been done in an attempt to synthesize olefinic  
8 block copolymers. The ideal catalyst system would produce a "living  
9 polymer." Unlike typical Ziegler-Natta polymerization processes  
10 living polymerization processes involve only initiation and  
11 propagation steps and are essentially devoid of terminating side  
12 reactions. This permits the synthesis of the predetermined and  
13 well-controlled structures required for effective block  
14 copolymerization. A polymer created in a "living" system can have an  
15 extremely narrow distribution of molecular weight and be essentially  
16 monodisperse. The living polymer technique is uniquely suited for the  
17 preparation of block copolymers. Living catalyst systems are  
18 characterized by an initiation rate which is considerably higher than  
19 the propagation rate, and the absence of termination or transfer  
20 reactions. In addition, these systems are characterized by the  
21 presence of a single type of active site.

22 Anionic polymerization routes to ideal olefinic block  
23 copolymers have been much studied. Butadiene-isoprene block  
24 copolymers have been synthesized using the sequential addition  
25 technique. In sequential addition, a certain amount of one of the  
26 monomers is contacted with the catalyst. Once the monomer has reacted  
27 to extinction, forming the first block, a certain amount of the second  
28 monomer species is introduced and allowed to react to form the second  
29 block. The process may be repeated as desired using the same or other  
30 anionically polymerizable monomers.

31 Ethylene and other alpha-olefins such as propylene and butene  
32 are not directly block polymerizable by anionic techniques. Another  
33 technique is described by Falk and Schlott in Macromolecules, 1971 4,  
34 152. The first step in the procedure involves preparing block  
35 polymers containing polybutadiene and polyisoprene using anionic

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1 techniques. The low pressure catalytic hydrogenation of the block  
2 polymer obtains the saturated block polymer.

3 The anionic routes to ideal olefinic block copolymers provide  
4 a clean route to model block copolymers. However, the method is  
5 impractical and is not sufficiently versatile for commercial  
6 purposes. For example, the anionic route cannot be used to synthesize  
7 HDPE or isotactic polypropylene (i-PP) segments.

8 A coordination technique which has been used to synthesize  
9 block copolymers involves the use of vanadium catalysts at low  
10 temperatures. Doi et. al., in Macromolecules, 1986, 19, 2896, showed  
11 that a catalyst prepared from  
12 tris(2-methyl-1,3-butanedionato)vanadium and  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  in  
13 toluene has high reactivity in the living coordination polymerization  
14 of propene and that a well-defined diblock copolymer of polypropylene  
15 and ethylene-propylene rubber can be prepared by adding ethylene  
16 monomer during the living polymerization of propene.

17 While the Doi technique has the advantage over the anionic  
18 routes of dispensing with the hydrogenation step, it does require very  
19 low temperatures. The block copolymerizations carried out by Doi et.  
20 al. were performed at -70 and -60 C. Doi also reported, in W.  
21 Kaminsky and H. Sinn (Eds.), Transition Metals and Organometallics as  
22 Catalysts for Olefin Polymerization, Springer-Verlag 1988, the living  
23 copolymerization, at -78 C, of propylene with 1,5-hexadiene. An  
24 additional disadvantage of the technique is that it cannot be used to  
25 produce i-PP. Furthermore, and no reports of the production of high  
26 density polyethylene (HDPE) via this method have appeared in the  
27 literature. The catalyst itself is poorly characterized and unstable.

28 Many claims in the prior art have been made for the  
29 production of block polymers in the presence of Ziegler-Natta type  
30 catalysts. For example, JP63-712 to Mitsubishi Petrochemicals claims  
31 a method of producing a propylene block copolymer using a catalyst  
32 including a solid titanium component containing magnesium, titanium,  
33 halogen and an electron-donor with an organo-aluminum cocatalyst to  
34 prepare homopolypropylene in a first stage reaction, following which  
35 in a second stage of reaction bis(cyclopentadienyl) titanium

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1 dichloride is added and polymerization is continued in the presence of  
2 added ethylene. The propylene block copolymers produced are said to  
3 have high rigidity and impact strength and good molding properties.

4 U.S. Patent 4,408,019 to Blunt relates to the use of a  
5 catalyst-activator system wherein titanium is the sole metal component  
6 to produce block copolymers of ethylene and propylene. The block  
7 copolymers have the general formula  $(AB)_n A$  wherein A is a  
8 crystalline polypropylene block, each B is a random ethylene-propylene  
9 copolymer block, and n is an integer from 1 to about 12. The  
10 catalyst-activator is described as a combination of titanium  
11 trichloride as the catalyst and

12 dimethylbis(methylcyclopentadienyl)titanium as an activator. The  
13 amount of ethylene in the block polymer is typically 40-65 wt.% with  
14 5-15 wt.% present in the ethylene-propylene segments. The  
15 thermoplastic block polymers are said to have superior tensile  
16 strength and lower compression set than prior art block polymers. In  
17 discussing prior art catalysts, Blunt observes that the production of  
18 a true block polymer is dependent upon there being no permanent  
19 interruption in the growth of any given polymer chain until all of the  
20 blocks have been completed. Moreover, Blunt states that the  
21 traditional Ziegler-Natta catalysts based on titanium halides in  
22 conjunction with alkylaluminum compounds do not provide a sufficiently  
23 long chain lifetime to permit the formation of block copolymers of  
24 more than two copolymer blocks.

25 While many patents and publications claim the synthesis of  
26 block copolymers from ethylene and propylene, there is no evidence  
27 that these products were obtained as well defined block polymers. The  
28 known kinetic features of heterogeneous Ziegler-Natta catalysts  
29 suggest that it is unlikely that block polymers were synthesized in  
30 high concentrations. (J. Boor, Ziegler-Natta Catalysts and  
31 Polymerizations, Academic Press 1979). According to Boor, the  
32 reported propylene and ethylene block copolymers are most likely  
33 mixtures of largely isotactic polypropylene, polyethylene, and either  
34 random, block, or tapered copolymers which are present in low  
35 concentrations, in the range of 0 to 20%.

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1           As reasons for his conclusion, Boor lists a large number of  
2 inherent barriers which must be overcome in using known Ziegler-Natta  
3 catalysts to synthesize block copolymers. For example, to synthesize  
4 ethylene/ $\alpha$ -olefins block copolymers the following conditions must be  
5 satisfied: 1) all of the Ti centers must become active  
6 simultaneously; 2) all the Ti centers must stay alive during the  
7 polymerization; 3) all the Ti centers must have equal activities for  
8 polymerizing propylene and ethylene; 4) all the Ti centers must be  
9 equally accessible to the available olefin molecules; 5) the  
10 cross-over propagation rates must be high for Ti-propylene centers to  
11 be efficiently converted into Ti-polyethylene centers; 6) the centers  
12 must be isotactic-specific for propylene polymerization and polymerize  
13 all ethylene molecules to a linear polymer.

14           Several difficulties arise in the use of known catalysts for  
15 the block copolymerization of olefins. Among those are the fact that  
16 conventional catalysts are typically multi-sited, and a significant  
17 fraction of the active sites are unstable. This leads to random chain  
18 initiation and termination which, in turn, lowers the theoretical  
19 block copolymer yield. What is desired, and what practice of this  
20 invention provides, is a catalyst system with well-characterized  
21 structure and reactivity which has a single active site. The system  
22 should have well-defined and stable polymerization kinetics and be  
23 free of aluminum alkyls or other chain transfer agents.

#### SUMMARY OF THE INVENTION

24           The invention comprises a process for the production of novel  
25 block copolymers of ethylene with an  $\alpha$ -olefin and the polymers  
26 obtained therefrom. The process includes sequentially contacting  
27 ethylene with an  $\alpha$ -olefin monomer in a suitable solvent at about 0°C  
28 in the presence of an ionic catalyst to produce a block copolymer.  
29 Thus, for example, when a-PP-HDPE diblock is produced, the process  
30 provides a diblock copolymer yield of 40-70%. The molecular weight of  
31 the block copolymer may be controlled by varying the  
32 catalyst-to-monomer ratio. The ionic catalyst which is a critical  
33 component of the inventive polymerization process, comprises the



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1 reaction product of a first component which is a bis(cyclopentadienyl)  
2 derivative of a metal of Group IV-B of the Periodic Table of the  
3 Elements, which metal is capable of forming a cation formally having a  
4 coordination number of 3 and a valence of +4; and at least one second  
5 component comprising a cation capable of donating a proton and a  
6 compatible non-coordinating anion which anion is bulky and labile, and  
7 capable of stabilizing the Group IV-B metal cation without interfering  
8 with the ability of said Group IV-B metal cation, or its decomposition  
9 product, to polymerize  $\alpha$ -olefins to form tapered polymers and  
10 multiblock polymers such as di- and tri-block homo-, and copolymers of  
11 ethylene and propylene with one or more other alpha-olefins.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

12 The invention provides (1) novel non-random di-, tri-, and  
13 multi-block copolymers and tapered copolymers of ethylene, 1-olefins,  
14 diolefins, cyclic olefins, acetylenes and other unsaturated monomers;  
15 and (2) the processes for polymerizing said non-random copolymers.

#### Ionic Catalyst System - General Description

16 The process of this invention is practiced with that class of  
17 ionic catalysts referred to, disclosed, and described in our copending  
18 U.S. Patent Application Nos. 133,052 and 133,480. The ionic catalyst  
19 is prepared by combining at least two components. The first of these  
20 is a bis(cyclopentadienyl) derivative of a Group IV-B metal compound  
21 containing at least one ligand which will combine with the second  
22 component or at least a portion thereof such as a cation portion  
23 thereof. The second component is an ion-exchange compound comprising  
24 a cation which will irreversibly react with at least one ligand  
25 contained in said Group IV-B metal compound and a noncoordinating  
26 anion which is bulky, labile, and stable. Upon combination of the  
27 first and second components, the cation of the second component reacts  
28 with one of the ligands of the first component, thereby generating an  
29 ion pair consisting of a Group IV-B metal cation with a formal  
30 coordination number of 3 and a valence of +4 and the aforementioned  
31 anion, which anion is compatible with and non-coordinating towards the

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1 metal cation formed from the first component. The anion of the  
2 second compound must be capable of stabilizing the Group IV-B  
3 metal cation complex without interfering with the Group IV-B metal  
4 cation's or its composition product's ability to function as a  
5 catalyst and must be sufficiently labile to permit displacement by  
6 an olefin, diolefin or an acetylenically unsaturated monomer  
7 during polymerization.

A. The Metallocene Component

8 The Group IV-B metal compounds; i.e., titanium, zirconium  
9 and hafnium metallocene compounds, useful as first compounds in  
10 the preparation of the improved catalyst of this invention are  
11 bis(cyclopentadienyl) derivatives of titanium, zirconium and  
12 hafnium. In general, useful titanocene, zirconocenes and  
13 hafnocenes may be represented by the following general formulae:

- 14 1.  $(A-Cp)MX_1X_2$
- 15 2.  $(A-Cp)MX'_1X'_2$
- 16 3.  $(A-Cp)ML$
- 17 4.  $(Cp^*)(CpR)MX_1$

18 wherein "Cp" represents a cyclopentadienyl radical which may be  
19 substituted or unsubstituted, and"

20 (A-cp) is either  $(Cp)(Cp^*)$  or  $Cp-A'-Cp^*$  and Cp and  $Cp^*$  are  
21 the same or different cyclopentadienyl ring substituted with  
22 from zero to five substituent groups R.

23 The substituent groups R may be, independently, selected  
24 from a wide variety of classes of radical groups which form  
25 covalent bonds to the carbon atoms of the Cp-rings. These  
26 substituents act to modify the catalyst behavior by affecting the  
27 symmetry, sterics, and electronics of the transition metal center.

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1 Illustrative but not limiting examples of suitable R substituents  
2 include hydrocarbyl radicals containing from 1 to 50 carbon atoms;  
3 substituted hydrocarbyl radicals wherein one or more of the  
4 hydrogen atoms is replaced by a halogen radical, an amido radical  
5 ( $X_1X_2N\cdot$ ), a phosphido radical ( $X_1X_2P\cdot$ ), an alkoxy radical ( $X_1O\cdot$ ) or  
6 any other radical containing Lewis acidic or basic functionality;  
7 hydrocarbyl substituted metalloid radicals wherein the metalloid  
8 is selected from the Group IV-A of the Periodic Table of elements;  
9 halogen radicals, amido radicals ( $X_1X_2N\cdot$ ), phosphido radicals  
10 ( $X_1X_2P\cdot$ ), alkoxy radicals ( $X_1O\cdot$ ), alkylborido radicals ( $X_1X_2B\cdot$ ), or  
11 any other radical containing Lewis acidic or basic functionality;  
12 or Cp and/or Cp\* are a cyclopentadienyl ring in which two adjacent  
13 R groups are joined forming a C<sub>4</sub> to C<sub>20</sub> ring to give a saturated  
14 or unsaturated polycyclic cyclopentadienyl ligand such as indenyl,  
15 tetrahydroindenyl, fluorenyl, or octahydrofluorenyl; A' is a  
16 covalent bridging group between the two cyclopentadienyl groups; M  
17 is titanium, zirconium or hafnium; L is an olefin, diolefin or  
18 aryne ligand; X<sub>1</sub> and X<sub>2</sub> are, independently, selected from the  
19 group consisting of hydride radicals, hydrocarbyl radicals having  
20 from 1 to about 20 carbon atoms, hydrocarbyl radicals wherein one  
21 or more of the hydrogen atoms are replaced with a halogen atom,  
22 organometalloid radicals comprising a Group IV-A element wherein  
23 each of the hydrocarbyl substitutions contained in the organic  
24 portion of said organometalloid independently contain from 1 to  
25 about 20 carbon atoms and the like; X'<sub>1</sub> and X'<sub>2</sub> are joined and  
26 bound to the metal atom to form a metallacycle, in which the metal  
27 atom, X'<sub>1</sub> and X'<sub>2</sub> form a hydrocarbocyclic ring containing from  
28 about 3 to about 20 carbon atoms; and R is a substituent,  
29 preferably a hydrocarbyl substituent, on one of the  
30 cyclopentadienyl radicals which is also bound to the metal atom.

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1           Illustrative, but not limiting examples of  
2 bis(cyclopentadienyl)zirconium compounds which may be used in the  
3 preparation of the improved catalyst of this invention are  
4 dihydrocarbyl-substituted bis(cyclopentadienyl)zirconium compounds  
5 such as bis(cyclopentadienyl)zirconium dimethyl,  
6 bis(cyclopentadienyl)zirconium diethyl, bis(cyclopentadienyl)zirconium  
7 dipropyl, bis(cyclopentadienyl)zirconium dibutyl,  
8 bis(cyclopentadienyl)zirconium diphenyl,  
9 bis(cyclopentadienyl)zirconium dineopentyl,  
10 bis(cyclopentadienyl)zirconium di(m-tolyl),  
11 bis(cyclopentadienyl)zirconium di(p-tolyl) and the like;  
12 (monohydrocarbyl-substituted cyclopentadienyl)zirconium compounds such  
13 as (methylcyclopentadienyl)(cyclopentadienyl) and  
14 bis(methylcyclopentadienyl)zirconium dimethyl, (ethylcyclopentadienyl)  
15 (cyclopentadienyl) and bis(ethylcyclopentadienyl)zirconium dimethyl,  
16 (propylcyclopentadienyl)(cyclopentadienyl) and  
17 bis(propylcyclopentadienyl)zirconium dimethyl,  
18 (n-butylcyclopentadienyl)(cyclopentadienyl) and  
19 bis(n-butylcyclopentadienyl)zirconium dimethyl,  
20 (t-butylcyclopentadienyl)(cyclopentadienyl) and  
21 bis(t-butylcyclopentadienyl)zirconium dimethyl,  
22 (cyclohexylmethylcyclopentadienyl)(cyclopentadienyl) and  
23 bis(cyclohexylmethylcyclopentadienyl)zirconium dimethyl,  
24 (benzylcyclopentadienyl)(cyclopentadienyl) and  
25 bis(benzylcyclopentadienyl)zirconium dimethyl,  
26 (diphenylmethylcyclopentadienyl)(cyclopentadienyl) and  
27 bis(diphenylmethylcyclopentadienyl)zirconium dimethyl,  
28 (methylcyclopentadienyl)(cyclopentadienyl) and  
29 bis(methylcyclopentadienyl)zirconium dihydride,  
30 (ethylcyclopentadienyl)(cyclopentadienyl) and  
31 bis(ethylcyclopentadienyl)zirconium dihydride,  
32 (propylcyclopentadienyl)(cyclopentadienyl) and  
33 bis(propylcyclopentadienyl)zirconium dihydride,  
34 (n-butylcyclopentadienyl)(cyclopentadienyl) and  
35 bis(n-butylcyclopentadienyl)zirconium dihydride,  
36 (t-butylcyclopentadienyl)(cyclopentadienyl) and

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1 bis(t-butylcyclopentadienyl)zirconium dihydride,  
2 (cyclohexylmethylcyclopentadienyl)(cyclopentadienyl) and  
3 bis(cyclohexylmethylcyclopentadienyl)zirconium dihydride,  
4 (benzylcyclopentadienyl)(cyclopentadienyl) and  
5 bis(benzylcyclopentadienyl)zirconium dihydride,  
6 (diphenylmethylcyclopentadienyl)(cyclopentadienyl) and  
7 bis(diphenylmethylcyclopentadienyl)zirconium dihydride and the like;  
8 (polyhydrocarbyl-substituted-cyclopentadienyl) zirconium compounds  
9 such as (dimethylcyclopentadienyl) (cyclopentadienyl) and  
10 bis(dimethylcyclopentadienyl) zirconium dimethyl,  
11 (trimethylcyclopentadienyl) (cyclopentadienyl) and  
12 bis(trimethylcyclopentadienyl) zirconium dimethyl,  
13 (tetramethylcyclopentadienyl) (cyclopentadienyl) and  
14 bis(tetramethylcyclopentadienyl) zirconium dimethyl,  
15 (permethylcyclopentadienyl) (cyclopentadienyl) and  
16 bis(permethylcyclopentadienyl) zirconium dimethyl,  
17 (ethyltetramethylcyclopentadienyl) (cyclopentadienyl) and  
18 bis(ethyltetramethylcyclopentadienyl) zirconium dimethyl,  
19 (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium dimethyl,  
20 (dimethylcyclopentadienyl) (cyclopentadienyl) and  
21 bis(dimethylcyclopentadienyl) zirconium dihydride,  
22 (trimethylcyclopentadienyl) (cyclopentadienyl) and  
23 bis(trimethylcyclopentadienyl) zirconium dihydride,  
24 (tetramethylcyclopentadienyl) (cyclopentadienyl) and  
25 bis(tetramethylcyclopentadienyl)zirconium dihydride,  
26 (permethylcyclopentadienyl) (cyclopentadienyl) and  
27 bis(permethylcyclopentadienyl)zirconium dihydride,  
28 (ethyltetramethylcyclopentadienyl) (cyclopentadienyl) and  
29 bis(ethyltetramethylcyclopentadienyl)zirconium dihydride,  
30 (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium  
31 (propylcyclopentadienyl) (cyclopentadienyl) and  
32 bis(propylcyclopentadienyl)zirconium dihydride,  
33 (n-butylcyclopentadienyl) (cyclopentadienyl) and  
34 bis(n-butylcyclopentadienyl)zirconium dihydride,  
35 (t-butylcyclopentadienyl) (cyclopentadienyl) and

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1 bis(t-butylcyclopentadienyl)zirconium dihydride,  
2 (cyclohexylmethylcyclopentadienyl) (cyclopentadienyl) and  
3 bis(cyclohexylmethylcyclopentadienyl)zirconium dihydride,  
4 (benzylcyclopentadienyl) (cyclopentadienyl) and  
5 bis(benzylcyclopentadienyl)zirconium dihydride,  
6 (diphenylmethylcyclopentadienyl) (cyclopentadienyl) and  
7 bis(diphenylmethylcyclopentadienyl)zirconium dihydride and the like;  
8 (polyhydrocarbyl-substituted-cyclopentadienyl) zirconium compounds  
9 such as (dimethylcyclopentadienyl) (cyclopentadienyl) and  
10 bis(dimethylcyclopentadienyl) zirconium dimethyl,  
11 (trimethylcyclopentadienyl) (cyclopentadienyl) and  
12 bis(trimethylcyclopentadienyl) zirconium dimethyl,  
13 (tetramethylcyclopentadienyl) (cyclopentadienyl) and  
14 bis(tetramethylcyclopentadienyl) zirconium dimethyl,  
15 (permethylcyclopentadienyl) (cyclopentadienyl) and  
16 bis(permethylcyclopentadienyl) zirconium dimethyl,  
17 (ethyltetramethylcyclopentadienyl) (cyclopentadienyl) and  
18 bis(ethyltetramethylcyclopentadienyl)zirconium dimethyl,  
19 (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium dimethyl,  
20 (dimethylcyclopentadienyl)(cyclopentadienyl) and  
21 bis(dimethylcyclopentadienyl)zirconium dihydride,  
22 (trimethylcyclopentadienyl) (cyclopentadienyl) and  
23 bis(trimethylcyclopentadienyl)zirconium dihydride,  
24 (tetramethylcyclopentadienyl) (cyclopentadienyl) and  
25 bis(tetramethylcyclopentadienyl)zirconium dihydride,  
26 (permethylcyclopentadienyl)(cyclopentadienyl) and  
27 bis(permethylcyclopentadienyl)zirconium dihydride,  
28 (ethyltetramethylcyclopentadienyl)(cyclopentadienyl) and  
29 bis(ethyltetramethylcyclopentadienyl)zirconium dihydride,  
30 (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium dihydride and  
31 the like; (metal hydrocarbyl-substituted cyclopentadienyl)zirconium  
32 compounds such as (trimethylsilylcyclopentadienyl)(cyclopentadienyl)  
33 and bis(trimethylsilylcyclopentadienyl)zirconium dimethyl,  
34 (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and  
35 bis(trimethylgermylcyclopentadienyl)zirconium dimethyl,

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1 (trimethylstannylcyclopentadienyl)(cyclopentadienyl) and  
2 bis(trimethylstannylcyclopentadienyl)zirconium dimethyl,  
3 (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and  
4 bis(trimethylplumbylcyclopentadienyl)zirconium dimethyl,  
5 (trimethylsilylcyclopentadienyl)(cyclopentadienyl) and  
6 bis(trimethylsilylcyclopentadienyl)zirconium dihydride,  
7 (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and  
8 bis(trimethylgermylcyclopentadienyl)zirconium dihydride,  
9 (trimethylstannylcyclopentadienyl)(cyclopentadienyl) and  
10 bis(trimethylstannylcyclopentadienyl)zirconium dihydride,  
11 (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and  
12 bis(trimethylplumbylcyclopentadienyl)zirconium dihydride and the like;  
13 (halogen-substituted-cyclopentadienyl) zirconium compounds such as  
14 (trifluoromethylcyclopentadienyl)(cyclopentadienyl) and  
15 bis(trifluoromethylcyclopentadienyl)zirconium dimethyl  
16 (trifluoromethylcyclopentadienyl)(cyclopentadienyl) and  
17 bis(trifluoromethylcyclopentadienyl)zirconium dihydride and the like;  
18 silyl-substituted bis(cyclopentadienyl) zirconium compounds such as  
19 bis(cyclopentadienyl) (trimethylsilyl)(methyl)zirconium,  
20 bis(cyclopentadienyl) (triphenylsilyl)(methyl)zirconium,  
21 bis(cyclopentadienyl) [tris(dimethylsilyl)silyl](methyl)zirconium,  
22 bis(cyclopentadienyl)[bis(mesityl)silyl](methyl)zirconium,  
23 bis(cyclopentadienyl)(trimethylsilyl)trimethylsilylmethyl) zirconium,  
24 bis(cyclopentadienyl) (trimethylsilylbenzyl) and the like;  
25 (bridged-cyclopentadienyl)zirconium compounds such as methylene  
26 bis(cyclopentadienyl)zirconium dimethyl,  
27 methylene(cyclopentadienyl)zirconium dimethyl, ethylene  
28 bis(cyclopentadienyl)zirconium dimethyl, dimethylsilyl  
29 bis(cyclopentadienyl)zirconium dihydride, ethylene  
30 bis(cyclopentadienyl)zirconium dihydride and dimethylsilyl  
31 bis(cyclopentadienyl)zirconium dihydride and the like; chiral and  
32 C<sub>2</sub>-symmetion compounds; "zirconacycles": assymmetrically  
33 bridged-dicyclopentadienyl compounds such as  
34 methylene(cyclopentadienyl)(1-fluorenyl)zirconium dimethyl,  
35 dimethylsily(cyclopentadienyl)(1-fluorenyl)zirconium dihydride,

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1 diphenylmethylene(cyclopentadienyl)(1-fluorenyl)zirconium dimethyl,  
2 isopropyl(cyclopentadienyl)(1-fluorenyl)zirconium dimethyl,  
3 isopropyl(cyclopentadienyl)(1-octahydrofluorenyl)zirconium dihydride,  
4 dimethylsilyl(methylcyclopentadienyl)(1-fluorenyl)zirconium dihydride,  
5 methylene(cyclopentadienyl(tetramethylcyclopentadienyl)zirconium  
6 dimethyl and the like; racemic and meso isomers of symmetrically  
7 bridged substituted dicyclopentadienyl compounds such as  
8 ethylenebis(indenyl)zirconium dimethyl,  
9 dimethylsilylbis(indenyl)zirconium dimethyl,  
10 ethylenebis(tetrahydroindenyl)zirconium dimethyl,  
11 dimethylsilylbis(3-trimethylsilylcyclopentadienyl)zirconium dihydride  
12 and the like; zirconacycles such as bis(pentamethylcyclopentadienyl)  
13 zirconacyclobutane, bis(pentamethylcyclopentadienyl)  
14 zirconacyclopentane, bis(cyclopentadienyl)zirconaindane,  
15 1-bis(cyclopentadienyl)zircona-3-dimethylsila-cyclobutane and the  
16 like; olefin, diolefin and aryne ligand substituted  
17 bis(cyclopentadienyl)zirconium compounds such as bis(cyclopentadienyl)  
18 (1,3-butadiene)zirconium, bis(cyclopentadienyl)  
19 (2,3-dimethyl-1,3-butadiene)zirconium,  
20 bis(pentamethylcyclopentadienyl)(benzyne)zirconium and the like;  
21 (hydrocarbyl)(hydride) bis(cyclopentadienyl)zirconium compounds such  
22 as bis(pentamethylcyclopentadienyl)zirconium (phenyl)(hydride),  
23 bis(pentamethylcyclopentadienyl)zirconium (methyl)(hydride) and the  
24 like; and bis(cyclopentadienyl) zirconium compounds in which a  
25 substituent on the cyclopentadienyl radical is bound to the metal such  
26 as (pentamethylcyclopentadienyl)  
27 (tetramethylcyclopentadienylmethylene) zirconium hydride,  
28 (pentamethylcyclopentadienyl)  
29 (tetramethylcyclopentadienylmethylene)zirconium phenyl and the like.  
30 A similar list of illustrative bis(cyclopentadienyl) hafnium  
31 and bis(cyclopentadienyl)titanium compounds could be made, but since  
32 the lists would be nearly identical to that already presented with  
33 respect to bis(cyclopentadienyl)zirconium compounds, such lists are  
34 not deemed essential to a complete disclosure. Other  
35 bis(cyclopentadienyl)hafnium compounds and other  
36 bis(cyclopentadienyl)titanium compounds as well as other



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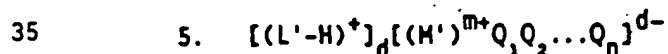
1 bis(cyclopentadienyl)zirconium compounds which are useful in the  
 2 catalyst compositions of this invention will, of course, be apparent  
 3 to those skilled in the art.

4

#### 5 B. The Activator Component

6 Compounds useful as an activator component in the preparation  
 7 of the catalyst of this invention will comprise a cation, which is a  
 8 Bronsted acid capable of donating a proton, and a compatible  
 9 noncoordinating anion which anion is relatively large (bulky), capable  
 10 of stabilizing the active catalyst species (the Group IV-B cation)  
 11 which is formed when the two compounds are combined and said anion  
 12 will be sufficiently labile to be displaced by olefinic, diolefinic  
 13 and acetylenically unsaturated substrates or other neutral Lewis bases  
 14 such as ethers, nitriles and the like. In general, suitable anions for  
 15 the second component may be any stable and bulky anionic complex having  
 16 the following molecular attributes: 1) the anion should have a  
 17 molecular diameter greater than 4Å; 2) the anion should form stable  
 18 ammonium salts; 3) the negative charge on the anion should be  
 19 delocalized over the framework of the anion or be localized within the  
 20 core of the anion; 4) the anion should be a relatively poor  
 21 nucleophile; and 5) the anion should not be a powerful reducing or  
 22 oxidizing agent. Anions meeting these criteria - such as polynuclear  
 23 boranes, carboranes, metallacarboranes, polyoxoanions and anionic  
 24 coordination complexes are well described in the chemical literature.  
 25 Two classes of compatible non-coordinating anions meeting these criteria  
 26 have been disclosed in our copending US Patent Applications Nos. 133,052  
 27 and 133,480: 1) anionic coordination complexes comprising a plurality  
 28 of lipophilic radicals covalently coordinated to and shielding a central  
 29 charge-bearing metal or metalloid core, and 2) anions comprising a  
 30 plurality of boron atoms such as carboranes, metallacarboranes and  
 31 boranes.

32 In general, the activator compounds containing single anionic  
 33 coordination complexes which are useful in this invention may be  
 34 represented by the following general formula:



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1           Wherein:

2                 L' is a neutral Lewis base;

3                 H is a hydrogen atom;

4                 [L'-H] is a Bronsted acid;

5                 M' is a metal or metalloid selected from the Groups  
6 subtended by Groups V-B to V-A of the Periodic Table of the Elements;  
7 i.e., Groups V-B, VI-B, VII-B, VIII, I-B, II-B, III-A, IV-A, and V-A;

8                 Q<sub>1</sub> to Q<sub>n</sub> are selected, independently, from the  
9 time, hydrocarbyl radicals containing from 1 to about 20 carbon atoms,  
10 substituted-hydrocarbyl radicals, wherein one or more of the hydrogen  
11 atoms is replaced by a halogen atom, containing from 1 to about 20  
12 carbon atoms, hydrocarbyl-substituted metal (organometalloid) radicals  
13 wherein each hydrocarbyl substitution contains from 1 to about 20  
14 carbon atoms and said metal is selected from Group IV-A of the  
15 Periodic Table of the Elements and the like.

16           In general, Ar<sub>1</sub> and Ar<sub>2</sub> may, independently, be any  
17 aromatic or substituted-aromatic hydrocarbon radical containing from  
18 about 6 to about 20 carbon atoms. Suitable aromatic radicals include,  
19 but are not limited to, phenyl, naphthyl and anthracenyl radicals.  
20 Suitable substituents on the substituted-aromatic hydrocarbon  
21 radicals, include, but are not necessarily limited to, hydrocarbyl  
22 radicals, organometalloid radicals, alkoxy radicals, alkylamido  
23 radicals, fluoro and fluorohydrocarbyl radicals and the like such as  
24 those useful as X<sub>3</sub> and X<sub>4</sub>. The substituent may be ortho, meta  
25 or para, relative to the carbon atoms bonded to the boron atom. When  
26 either or both X<sub>3</sub> and X<sub>4</sub> are a hydrocarbyl radical, each may  
27 be the same or a different aromatic or substituted-aromatic radical as  
28 are Ar<sub>1</sub> and Ar<sub>2</sub>, or the same may be a straight or branched  
29 alkyl, alkenyl or alkynyl radical having from 1 to about 20 carbon  
30 atoms, a cyclic hydrocarbon radical having from about 5 to about 8  
31 carbon atoms or an alkyl-substituted cyclic hydrocarbon radical having  
32 from about 6 to about 20 carbon atoms. X<sub>3</sub> and X<sub>4</sub> may also,  
33 independently, be alkoxy or dialkylamido radicals wherein the alkyl  
34 portion of said alkoxy and dialkylamido radicals contain from 1 to  
35 about 20 carbon atoms, hydrocarbyl radicals and organometalloid  
36 radicals having from 1 to about 20 carbon atoms and the like. As

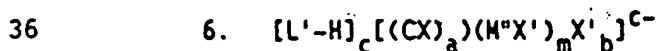
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1 indicated above, Ar<sub>1</sub> and Ar<sub>2</sub> may be linked to each other.  
 2 Similarly, either or both of Ar<sub>1</sub> and Ar<sub>2</sub> could be linked to  
 3 either X<sub>3</sub> or X<sub>4</sub>. Finally, X<sub>3</sub> or X<sub>4</sub> may also be linked  
 4 to each other through a suitable bridging group.

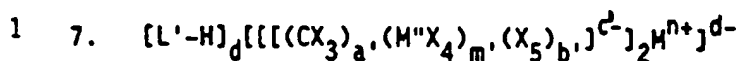
5 Illustrative, but not limiting, examples of boron compounds  
 6 which may be used as an activator component in the preparation of the  
 7 improved catalysts of this invention are trialkyl-substituted ammonium  
 8 salts such as triethylammonium tetra(phenyl)boron, tripropylammonium  
 9 tetra(phenyl)boron, tri(n-butyl)ammonium tetra(phenyl)boron,  
 10 trimethylammonium tetra(p-tolyl)boron, trimethylammonium  
 11 tetra(o-tolyl)boron, tributylammonium tetra(pentafluorophenyl)boron,  
 12 tripropylammonium tetra(o,p-dimethylphenyl)boron, tributylammonium  
 13 tetra(m,m-dimethylphenyl)boron, tributylammonium  
 14 tetra(p-tri-fluoromethylphenyl)boron, tri(n-butyl)ammonium  
 15 tetra(o-tolyl)boron and the like; N,N-dialkyl anilinium salts such as  
 16 N,N-dimethylanilinium tetra(pentafluoro phenyl)boron,  
 17 N,N-diethylanilinium tetra(phenyl)boron,  
 18 N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron and the like;  
 19 dialkyl ammonium salts such as di(i-propyl)ammonium  
 20 tetra(pentafluorophenyl)boron, dicyclohexylammonium tetra(phenyl)boron  
 21 and the like; and triaryl phosphonium salts such as  
 22 triphenylphosphonium tetra(phenyl)boron, tri(methylphenyl)phosphonium  
 23 tetra(phenyl)boron, tri(dimethylphenyl)phosphonium tetra(phenyl)boron  
 24 and the like.

25 Similar lists of suitable compounds containing other metals  
 26 and metalloids which are useful as activator components may be made,  
 27 but such lists are not deemed necessary to a complete disclosure. In  
 28 this regard, it should be noted that the foregoing list is not  
 29 intended to be exhaustive and that other useful boron compounds as  
 30 well as useful compounds containing other metals or metalloids would  
 31 be readily apparent to those skilled in the art from the foregoing  
 32 general equations.

33 Activator components based on anions which contain a  
 34 plurality of boron atoms may be represented by the following general  
 35 formulae:



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2    wherein  $[L'-H]$  is either  $H^+$ , ammonium or a substituted  
 3    ammonium cation having up to 3 hydrogen atoms replaced with a  
 4    hydrocarbyl radical containing from 1 to about 20 carbon atoms or a  
 5    substituted-hydrocarbyl radical, wherein one or more of the hydrogen  
 6    atoms is replaced by a halogen atom, containing from 1 to about 20  
 7    carbon atoms, phosphonium radicals, substituted-phosphonium  
 8    radicals having up to 3 hydrogen atoms replaced with a hydrocarbyl  
 9    radical containing from 1 to about 20 carbon atoms or a  
 10    substituted-hydrocarbyl radical, wherein 1 or more of the hydrogen  
 11    atoms is replaced by a halogen atom, containing from 1 to about 20  
 12    carbon atoms and the like; C is carbon;  $M''$  is boron or phosphorus;  
 13    each of  $X$ ,  $X'$ ,  $X''$ ,  $X_3$ ,  $X_4$  and  $X_5$  are radicals selected,  
 14    independently, from the group consisting of hydride radicals, halide  
 15    radicals, hydrocarbyl radicals containing from 1 to about 20 carbon  
 16    atoms, substituted-hydrocarbyl radicals, wherein one or more of the  
 17    hydrogen atoms is replaced by a halogen atom, containing from 1 to 20  
 18    carbon atoms, organometalloid radicals wherein each hydrocarbyl  
 19    substitution in the organo portion contains from 1 to about 20 carbon  
 20    atoms and said metal is selected from Group IV-A of the Periodic  
 21    Table of the Elements and the like;  $M$  is a transition metal; " $a$ " and  
 22    " $b$ " are integers  $\geq 0$ ; " $c$ " is an integer  $\geq 1$ ;  $a + b + c =$  an  
 23    even-numbered integer from 2 to about 8; and " $m$ " is an integer  
 24    ranging from 5 to about 22; " $a'$ " and " $b'$ " are the same or a different  
 25    integer  $\geq 0$ ; " $c'$ " is an integer  $\geq 2$ ;  $a' + b' + c' =$  an  
 26    even-numbered integer from 4 to about 8; " $m'$ " is an integer from 6 to  
 27    about 12; " $n$ " is an integer such that  $2c' - n = d$ ; and " $d$ " is an  
 28    integer greater than or equal to 1.

29            Illustrative, but not limiting, examples of second  
 30    components which can be used in preparing catalyst systems utilized  
 31    in the process of this invention wherein the anion of the second  
 32    component contains a plurality of metalloid atoms (as in formulae 5  
 33    and 6) are ammonium salts such as ammonium 1-carbadodecaborate (using  
 34    1-carbadodecaborate as an illustrative, but not limiting, counterion  
 35    for the ammonium cations listed below): monohydrocarbyl-substituted  
 36    ammonium salts such as methylammonium 1-carbadodecaborate,  
 37    ethylammonium 1-carbadodecaborate, propylammonium

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1 1-carbadodecaborate, isopropylammonium 1-carbadodecaborate,  
2 (n-butyl)ammonium 1-carbadodecaborate, anilinium 1-carbadodecaborate,  
3 and (p-tolyl)ammonium 1-carbadodecaborate and the like;  
4 dihydrocarbyl-substituted ammonium salts such as dimethylammonium  
5 1-carbadodecaborate, diethylammonium 1-carbadodecaborate,  
6 dipropylammonium 1-carbadodecaborate, diisopropylammonium  
7 1-carbadodecaborate, di(n-butyl) ammonium 1-carbadodecaborate,  
8 diphenylammonium 1-carbadodecaborate, di(p-tolyl)ammonium  
9 1-carbadodecaborate and the like; trihydrocarbyl-substituted ammonium  
10 salts such as trimethylammonium 1-carbadodecaborate, triethylammonium  
11 1-carbadodecaborate, tripropyl-ammonium 1-carbadodecaborate,  
12 tri(n-butyl) ammonium 1-carbadodecaborate, triphenylammonium  
13 1-carbadodecaborate, tri(p-tolyl)ammonium 1-carbadodecaborate,  
14 N,N-dimethylanilinium 1-carbadodecaborate, N,N-diethylanilinium  
15 1-carbadodecaborate and the like.

16 Illustrative, but not limiting examples of second compounds  
17 corresponding to Formula 5 [using tri(n-butyl)ammonium as an  
18 illustrative, but not limiting, counterion for the anions listed  
19 below] are salts of anions such as bis[tri(n-butyl)ammonium]  
20 nonaborate, bis[tri(n-butyl)ammonium]decaborate, bis[tri(n-butyl)  
21 ammonium]undecaborate, bis[tri(n-butyl)ammonium] dodecaborate,  
22 bis[tri(n-butyl)ammonium]decachlorodecaborate, tri(n-butyl)ammonium  
23 dodecachlorododecaborate, tri(n-butyl)ammonium 1-carbadecaborate,  
24 tri(n-butyl) ammonium 1-carbaundecaborate, tri(n-butyl)ammonium  
25 1-carbadodecaborate, tri(n-butyl)ammonium  
26 1-trimethylsilyl-1-carbadecaborate, tri(n-butyl)ammonium  
27 dibromo-1-carbadodecaborate and the like; borane and carborane  
28 complexes and salts of borane and carborane anions such as  
29 decaborane(14), 7,8-dicarbaundecaborane(13),  
30 2,7-dicarbaundecaborane(13),  
31 undecahydrido-7,8-dimethyl-7,8-dicarbaundecaborane,  
32 dodecahydrido-11-methyl-2,7-di-carbaundecaborane, tri(n-butyl)  
33 ammonium undecaborate(14), tri(n-butyl)ammonium  
34 6-carbadecaborate(12), tri(n-butyl)ammonium 7-carbaundecaborate(13),  
35 tri(n-butyl)ammonium 7,8-dicarbaundecaborate(12),

- 20 -

1 tri(n-butyl)ammonium 2,9-dicarbaundecaborate(12),  
2 tri(n-butyl)ammonium dodecahydrido-8-methyl-7,9-dicarbaundecaborate,  
3 tri(n-butyl)ammonium undecahydrido-8-ethyl-7,9-dicarbaundecaborate,  
4 tri(n-butyl) ammonium undecahydrido-8-butyl-7,9-dicarbaundecaborate,  
5 tri(n-butyl)ammonium undecahydrido-8-allyl-7,9-dicarbaundecaborate,  
6 tri(n-butyl)ammonium  
7 undecahydrido-9-trimethylsilyl-7,8-dicarbaundecaborate,  
8 tri(n-butyl)ammonium undecahydrido-4,6-dibromo-7-carbaundecaborate  
9 and the like; boranes and carboranes and salts of boranes and  
10 carboranes such as 4-carbanonaborane(14), 1,3-dicarbanonaborane(13),  
11 6,9-dicarbadeceborane(14),  
12 dodecahydrido-1-phenyl-1,3-dicarbanonaborane,  
13 dodecahydrido-1-methyl-1,3-dicarbanonaborane,  
14 undecahydrido-1,3-dimethyl-1,3-dicarbanonaborane and the like.  
15 Illustrative, but not limiting, examples of second compounds  
16 corresponding to Formula 7 [using tri(n-butyl)ammonium as an  
17 illustrative, but not limiting, counterion for the anions listed  
18 below] are salts of metallocarborane and metallocaborane anions such as  
19 tri(n-butyl)ammonium bis(nonahydrido-1,3-dicarbanonaborato)  
20 cobaltate(III), tri(n-butyl)ammonium  
21 bis(undeca-hydrido-7,8-dicarbaundecaborato)ferrate(III), tri(n-butyl)  
22 ammonium bis(undecahydrido-7,8-dicarbaundecaborato)cobaltate(III),  
23 tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaunaborato)  
24 nikelate(III), tri(n-butyl)ammonium bis(nonahydrido-7,  
25 8-dimethyl-7,8-dicarbaundecaborato)ferrate(III), tri(n-butyl)ammonium  
26 bis(nonahydrido-7,8-dimethyl-7,8-dicarbaundecaborato)chromate(III),  
27 tri(n-butyl)ammonium  
28 bis(tribromooctahydrido-7,8-dicarbaundecaborato)cobaltate(III),  
29 tri(n-butyl)ammonium bis(dodecahydridodicarbadeceborato)  
30 cobaltate(III), tris[tri(n-butyl)ammonium] bis  
31 (undecahydrido-7-carbaundecaborato)chromate(III),

- 21 -

1 bis[tri(n-butyl) ammonium]  
2 bis(undecahydrido-7-carbaundecaborato)manganate(IV),  
3 bis[tri(N-butyl)ammonium] bis(undecahydrido-7-carbaundecaborato)  
4 cobaltate(III), bis[tri (n-butyl)ammonium] .  
5 bis(undecahydrido-7-carbaundecaborato) nickelate(IV) and the like. A  
6 similar list of representative phosphonium compounds can be recited  
7 as illustrative second compounds, but for the sake of brevity, it is  
8 simply noted that the phosphonium and substituted-phosphonium salts  
9 corresponding to the listed ammonium and substituted-ammonium salts  
10 could be used as second compounds in the present invention.

#### Choice of Metallocene-Activator Pairs

11 In general, and while most metallocene components identified  
12 above may be combined with most activator components identified above  
13 to produce an active olefin polymerization catalyst, it is important  
14 for continuity of the polymerization operations that either the metal  
15 cation initially formed from the metallocene component or a  
16 decomposition product thereof be a relatively stable catalyst. It is  
17 also important that the anion of the activator compound be stable to  
18 hydrolysis when an ammonium salt is used. Further, it is important  
19 that the acidity of the activator component be sufficient, relative  
20 to the metallocene component, to facilitate the needed proton  
21 transfer. Activator compounds containing aryl-ammonium salts such as  
22 N,N-dimethylanilium are more acidic than trialkylammonium salts and  
23 therefore are useful with a wider variety of metallocene components.  
24 The basicity of the metal complex must also be sufficient to  
25 facilitate the needed proton transfer. In general,  
26 bis(cyclopentadienyl)metal compounds which can be hydrolyzed by  
27 aqueous solutions can be considered suitable as metallocene  
28 components to form the catalysts described herein.

29 The chemical reactions which occur may be represented by  
30 reference to the general formulae set forth herein as follows:

- 22 -

- 1 A.  $(A-Cp)MX_1X_2 + [L'-H]^+[B']^- \rightarrow [(A-Cp)MX_1]^+[B']^- + HX_2 + L'$  or  
 2  $[(A-Cp)MX_2]^+[B']^- + HX_1 + L'$   
 3 B.  $(A-Cp)\overline{MX'_1X'_2} + [L'-H]^+[B']^- \rightarrow [(A-Cp)MX'_1X'_2H]^+[B']^- + L'$  or  
 4  $[(A-Cp)MX'_2X'_1H]^+[B']^- + L'$   
 5 C.  $(A-Cp)ML + [L'-H]^+[B']^- \rightarrow [(A-Cp)M(LH)]^+[B']^- + L'$   
 6 D.  $(Cp^*)(\overline{RCp})MX_1 + [L'-H]^+[B']^- \rightarrow [(Cp^*)(HR-Cp)MX_1]^+[B']^- + L'$  or  
 7  $[(Cp^*)(\overline{R-Cp})M]^+[B']^- + HX_1 + L'$

8 In the foregoing reaction equations, the letters A-D  
 9 correspond to the numbers 1-4, respectively, set forth in combination  
 10 with the general equations for useful metallocene compounds. B'  
 11 represents a compatible ion corresponding to the general formulae  
 12 outlined in formulae 5, 6 and 7 above. When the metallocene and  
 13 activator components used to prepare the improved catalysts of the  
 14 present invention are combined in a suitable solvent or diluent, all  
 15 or a part of the cation of the activator (the acidic proton) combines  
 16 with one of the substituents on the metallocene compound. In the case  
 17 where the metallocene component has a formula corresponding to that of  
 18 general formula 1, a neutral compound is liberated, which neutral  
 19 compound either remains in solution or is liberated as a gas. In this  
 20 regard, it should be noted that if either  $X_1$  or  $X_2$  in the  
 21 metallocene component is a hydride, hydrogen gas may be liberated.  
 22 Similarly, if either  $X_1$  or  $X_2$  is a methyl radical, methane may  
 23 be liberated as a gas. In the cases where the first component has a  
 24 formula corresponding to those of general formulae 2, 3 or 4  
 25 (optional), one of the substituents on the metallocene component is  
 26 protonated but no substituent is liberated. In general, the stability  
 27 and rate of formation of the products in the foregoing reaction  
 28 equations will vary depending upon the choice of the solvent, the  
 29 acidity of the  $[L'-H]^+$  selected, the particular  $L'$ , the anion, the  
 30 cyclopentadienyl derivative of the metal selected.

31 With respect to the combination of the metallocene component  
 32 with the activator component to form a catalyst of this invention, it



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1 should be noted that the two compounds combined for preparation of the  
2 active catalyst must be selected so as to avoid transfer of a fragment  
3 of the anion to the metal cation, thereby forming a catalytically  
4 inactive species. This could be done by steric hindrance, resulting  
5 from substitutions on the cyclopentadienyl carbon atoms as well as  
6 substitutions on the non-coordinating anion.

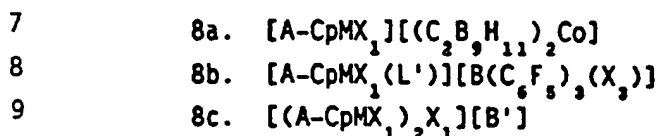
7 It follows, then, that the metallocene components comprising  
8 perhydrocarbyl-substituted cyclopentadienyl radicals could be  
9 effectively used with a broader range of activator compounds than  
10 could metallocene components comprising unsubstituted cyclopentadienyl  
11 radicals.

12 As the amount and size of the substitutions on the  
13 cyclopentadienyl radicals are reduced, however, more effective  
14 catalysts are obtained with activator compounds containing  
15 non-coordinating anions which are larger in size and more resistant to  
16 degradation. In the case where the non-coordinating anion is an  
17 anionic coordination complex, such as a tetraphenylboron derivative,  
18 substitutions on the phenyl rings can be used to prevent the transfer  
19 of a proton or an entire phenyl group from the anion to the metal.  
20 This can be accomplished by alkyl substitution in the ortho positions  
21 of the phenyl groups, or, more preferably, by perfluoro-substitutions  
22 on the anion. Thus, anionic coordination complexes containing  
23 perfluorophenyl-, trifluoromethylphenyl-, or bis-trifluoromethylphenyl  
24 rings are preferred for this subgenus of activator components. When  
25 the non-coordinating anion contains a plurality of boron atoms as  
26 described in general formulae 6 and 7, more effective catalysts are  
27 obtained with activator compounds containing larger anions, such as  
28 those encompassed by Equation 7 and those having larger  $m$  values in  
29 Equation 6. In these cases it is further preferable when using second  
30 compounds which are encompassed by Equation 6, that  $a + b + c = 2$ .  
31 Second compounds in which  $a + b + c =$  even-numbered integers of 4 or  
32 more have acidic B-H-B moieties which can react further with the metal  
33 cation formed, leading to catalytically inactive compounds.

34 As indicated supra, most metallocene compounds will combine  
35 with most activator compounds to give an active polymerization

- 24 -

1 catalyst. The initially formed catalyst is not, however, always  
 2 sufficiently stable as to permit its separation and subsequent  
 3 identification. However, catalysts which are thermally stable are  
 4 preferred for the production of block or tapered copolymers. Three  
 5 structurally distinct forms of thermally stable ionic catalysts have  
 6 been identified by NMR spectroscopy and are shown below in equation 8.



10 In the foregoing reactions the symbols A-Cp, M,  $X_1$ ,  $L'$  and  $X_2$   
 11 correspond to the definitions set forth in equations 1-4 and 5-5a,  
 12 respectively;  $B'$  represents a compatible non-coordinating anion  
 13 corresponding to the general formulae set forth in equations 5, 6 and  
 14 7. In example 8a, NMR spectroscopy indicates that the  
 15 metallacarborane anion is weakly bound to the metal center; the  
 16 biproduct  $L'$  does not form an observable coordination complex with the  
 17 metallocene center. In 8b, NMR experiments indicate that the  
 18 fluorinated boron anion is completely non-coordinating and that  $L'$ ,  
 19 weakly coordinates to and stabilizes the metallocene cation when the  
 20 tertiary amine ( $L'$ ) is an aniline derivative. The ability of  $L'$  to  
 21 coordinate to the metal is important to the stability of the catalyst  
 22 systems which have highly noncoordinating anions. The Lewis basicity  
 23 of the  $L'$  can affect the rate of polymerization and other  
 24 polymerization parameters. Experience has shown that when the bulk of  
 25 the amine or the metallocene cation is increased by substitutions on  
 26 the nitrogen atom or the cyclopentadienyl ligands respectively, the  
 27 ability for the amine to coordinate to the metal center decreases.  
 28 Addition of excess metallocene  $ACpM(X_1)_2$  to 8a or 8b results  
 29 in displacement of the anion in 8a or the aniline ligand in 8b to form  
 30 a stable dimeric cation 8c.

- 25 -

1           Preferred Catalysts For the Production of Block and Tapered  
2 Copolymers

3           Ideal catalyst systems for the production of block copolymers  
4 are single-sited living catalysts. Living catalysts are those systems  
5 in which chain transfer is nonexistent and the rate of initiation is  
6 fast compared to propagation. Catalysts which have finite chain  
7 transfer rates may also be useful for the production of block and  
8 tapered copolymers if the rate of propagation is fast relative to  
9 termination. It is also important that the average chain lifetimes  
10 are reasonably long (minutes to hours) in order to permit adequate  
11 time for modifications of the reactor conditions (e.g. changing  
12 monomer feed streams). While most reasonably stable ionic catalysts  
13 described above will under suitable conditions produce block and/or  
14 tapered copolymers of nonpolar olefins, it is preferred that the  
15 catalyst be: 1) thermally stable (recoverable as a single  
16 organometallic complex), 2) versatile in terms of random copolymer  
17 synthesis (i.e. capable of preparing HDPE, i-PP, s-PP, EP-rubber,  
18 LLDPE etc.), 3) capable of producing high molecular weight polymers at  
19 reasonable temperatures and pressures, 4) high activity (fast  
20 propagation catalysts) and 5) slow in chain termination reactions so  
21 that few chains of polymer product are produced per hour per site.

22           Ionic catalysts of the form  $[A-CpMMe(L')][B(C_6F_5)_3(X)]$  are  
23 the preferred catalysts for the production of block and tapered  
24 copolymers of ethylene, 1-olefins, dienes, cyclic olefins and other  
25 unsaturated monomers. Ionic catalysts of this form where M = Hf are  
26 the most preferred catalyst systems because they are more stable,  
27 produce higher molecular weight copolymers, and have longer chain  
28 lifetimes than corresponding Zr or Ti-based systems. Polymerizations  
29 using hafnium systems of this form under standard random copolymer  
30 conditions as described in our copending U.S. Patent Application No.  
31 133,480 produce high molecular weight HDPE, LLDPE, a-PP, i-PP, s-PP,  
32 and EP-rubber at rates comparable to similar Zr-based catalysts.  
33 Tapered and block copolymers containing these segments can be  
34 produced using the appropriate hafnium ionic catalyst using the  
35 techniques and process conditions set forth in the following sections.

- 26 -

1           Processes For the Production of Block and Tapered Copolymers

2           Many procedures for modifying the reactor conditions and  
3 monomer feeds for the production of block copolymers have been  
4 developed and applied using conventional Ziegler-Natta catalysts.  
5 The patent literature concerning block copolymer from Ziegler-Natta  
6 catalysts disclose a variety of processes for altering reactor  
7 conditions. The processes include batch reactors and sequential  
8 additions techniques, series batch reactors, loop and tubular  
9 reactors, and fluidized bed reactors. A review of the processes and  
10 patents is given in chapter 4 of "Block Copolymers" [D. C. Allport  
11 and W. H. James; John Wiley and Sons, New York 1973]. As indicated  
12 supra, the application of these processes using conventional  
13 catalysts in general produces broad molecular weight distributions of  
14 poorly defined polymer blends. In principle, the catalysts of this  
15 invention can be used in any of the processes described above for the  
16 production well-defined block copolymers of higher purity than  
17 obtained using conventional Ziegler-Natta catalysts.

18           The most demanding process, that is the process which  
19 requires the longest chain lifetimes, is the sequential addition.  
20 When the catalyst or initiator produces growing chains with  
21 sufficiently long lifetimes, the sequential addition technique allows  
22 for the production of block copolymers having non-tapered transitions  
23 between different polymer segments. Sequential addition techniques  
24 are commonly used to produce styrenic block copolymers (Kraton for  
25 example) using anionic initiators.

26           In the first step of the sequential addition process  
27 employed in accordance with this invention the catalyst is placed in  
28 a well stirred batch reactor in a suitable solvent and first segment  
29 of the block copolymer is grown by adding a specific number of molar  
30 equivalents of monomer(s). The catalyst consumes all of the  
31 monomer(s) prior to addition of the second monomer(s) (a different  
32 set of monomers than in the first step). This procedure can be  
33 repeated to prepare multiblock copolymers.

Sequential Addition Conditions

34           For a given catalyst and target block or tapered copolymer a

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1 solvent, temperature and catalyst concentration must be chosen so  
2 that 1) narrow molecular weight distribution, high molecular weight  
3 copolymer segments can be synthesized; and 2) the molecular weight of  
4 the copolymer segments can be controlled by varying the  
5 catalyst-to-monomer molar ratio. Under these conditions the system  
6 is behaving in a quasilinging fashion (i.e. slow chain transfer) and  
7 narrow molecular weight block copolymers can be prepared in high  
8 yield. Methods for choosing the conditions for a particular catalyst  
9 system are given below.

#### Solvent

10 Preferably, the solvent should normally disperse or dissolve  
11 the catalyst to form a well-mixed system. The most preferred  
12 catalysts for block copolymer synthesis,  
13  $[\text{ACpHfMe}(\text{L}')][\text{B}(\text{C}_6\text{F}_5)_4]$ , are prepared in toluene and form non-miscible,  
14 toluene-dispersible phases. This two-component phase contains the  
15 catalyst and a particular amount of toluene; the concentration of  
16 toluene in the catalyst phase depends on temperature and the structure  
17 of the catalyst. Addition of an aliphatic  
18 hydrocarbon to the toluene-catalyst emulsion causes immediate  
19 precipitation of the catalyst from solution to give a soft waxy,  
20 non-dispersible catalyst deposit. While aliphatic hydrocarbons,  
21 fluorinated hydrocarbons, and chlorinated aromatic hydrocarbons may  
22 be used in this invention, the preferred solvents for the preparation  
23 of block copolymers from the most preferred catalysts are aromatic  
24 hydrocarbons such as toluene, xylene, ethyl benzene and the like.  
25 The lack of solubility or compatibility of the catalyst phase in the  
26 aromatic solvent does not present significant problems in terms of  
27 molecular weight broadening because the phase is highly dispersible  
28 even at lower temperatures.

#### Temperature

29 The reactor temperature strongly affects the yield of block  
30 copolymer and must be adjusted depending on the type and  
31 concentration of monomers and catalyst used. The general procedure  
32 for determining this condition is to 1) find the maximum temperature  
33 where high molecular weight polymer segments can be prepared and 2)

- 28 -

1 confirm the molecular weight is controlled by the catalyst-to-monomer  
2 ratio at this temperature. The general trend is that higher  
3 temperatures cause chain transfer to be more rapid relative to  
4 propagation and therefore give lower block copolymer yields. The  
5 process may be carried out at temperatures of  $-80^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ , however,  
6 it is preferred that the temperature be in the range of  $-10^{\circ}\text{C}$  to  
7  $20^{\circ}\text{C}$ .

#### Concentration of Catalyst

8 The concentration should be high enough to produce  
9 significant rates of polymerization under the generally low pressure  
10 conditions of sequential addition. The concentration should not be  
11 so high as to produce uncontrollable exotherms upon exposure to the  
12 monomer. The exotherm can be controlled, however, by adjusting the  
13 rate of monomer addition during the formation of a block segment.  
14 This level of control allows for a large range of acceptable  
15 catalysts concentrations. The process may be carried out at catalyst  
16 concentrations ranging from about  $6 \times 10^{-6}$  to about  $6 \times 10^{-2}$   
17 moles of catalyst/liter of solution, however it is preferred that  
18 catalyst levels be in the range of  $1 \times 10^{-4}$  to about  $3 \times 10^{-3}$   
19 moles of catalyst/liter of solution.

#### Monomer Concentration

20 The amount of monomer added depends on the molecular weight  
21 of the targeted polymer and the moles of active catalyst in the  
22 reactor. Molar ratios of monomer to catalyst may be in the range of  
23 about 10:1 to about 10,000:1. The monomers may be added quickly or  
24 may be metered in to the reactor to control exotherms.

#### Order of Monomer Addition

25 Precipitation of polymer (with catalyst attached) causes  
26 undesirable broadening of the molecular weight distribution due to  
27 mass transport limitations and poor mixing. It is therefore  
28 preferred to prepare the soluble block (generally the elastomeric  
29 segment) in the first stage of the reaction. Thus, as indicated in  
30 the examples, when ethylene is added in the first step in the  
31 synthesis of a HDPE-b-atactic-PP diblock copolymer the initially  
32 formed polyethylene precipitates with the catalyst and the final

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1 molecular weight distribution of crude block copolymer product is  
2 rather broad ( $M_w/M_n = 3.0$ ). Addition of propylene in the first step  
3 produces a system which remains homogeneous throughout the block  
4 copolymer synthesis, yielding a crude product having a much narrower  
5  $M_w/M_n = (1.7 - 1.8)$ .

#### Preparation of Tapered and Random Copolymers

6 Addition of stoichiometric amounts of a mixture of two  
7 olefins to the reactor under block copolymer conditions will  
8 naturally produce tapered copolymer because the monomers will  
9 generally have different reactivities with the catalyst. Thus, the  
10 head of the polymer will be rich in the more reactive comonomer while  
11 the polymer tail will contain larger amounts of the slower reacting  
12 comonomer. The extent of tapering will depend on magnitude of the  
13 difference of monomer reactivity. The extent of tapering can be  
14 controlled by metering the two monomers into the reactor at different  
15 rates.

16 Random copolymers such as non-crystalline ethylene-propylene  
17 rubber can be made under block copolymer conditions by adding the  
18 fast monomer (ethylene) to the catalyst/propylene mixture at a rate  
19 where the desired amount of ethylene has been added when all the  
20 propylene has been consumed. This procedure is exemplified for a  
21 ethylene-propylene elastomer containing 50 mole % propylene.

#### Block Copolymer Products

22 The novel polymer products of this invention are olefinic  
23 block and tapered copolymers having narrow molecular weight  
24 distributions and well defined di-, tri-, multiblock or tapered  
25 structures. The polymer segments which can be incorporated into  
26 these architectures include 1) elastomers such as atactic  
27 polypropylene, atactic poly-1-olefins, and ethylene/1-olefin  
28 copolymers wherein the ethylene comonomer is a  $C_3-C_{18}$   
29  $\alpha$ -olefin such as ethylene-propylene, ethylene butene, and  
30 ethylene-octene copolymers ethylene-propylene-diene terpolymers and  
31 other crosslinkable elastomeric olefins; 2) thermoplastics such as  
32 high density polyethylene, linear low density polyethylene having  
33 melting points from 80-135°C (e.g. ethylene-propylene and other

- 30 -

1 ethylene-1-olefin copolymers wherein each 1-olefin has from about 4  
2 to 20 carbon atoms), ethylene/diene copolymers such as  
3 ethylene/ethylidene-norbornene copolymers, isotactic polypropylene  
4 having melting points from 100°C-165°C, syndiotactic polypropylenes  
5 having melting points from 100°C-165°C, hemi-isotactic polypropylenes  
6 and other crystalline 1-olefin homo and copolymers; and 3) glasses  
7 such as homo-polycyclopentene, homopolynorbornene and the like. The  
8 average molecular weight of the polymer segments included in the  
9 novel block copolymers of this invention can be in the range of from  
10 100-1,000,000 daltons, preferably from 30,000 to 200,000 daltons.  
11 The molecular weight distributions (Mw/Mn) of the crude and/or  
12 fractionated block copolymer are in the range from about 1.0 to about  
13 5.0, preferable from about 1.1 to about 2.0. As indicated above and  
14 in the examples following the percentage of block copolymer in the  
15 crude product can vary from about 1% to 100%, preferably from about  
16 50% to about 90% depending on the application and the conditions of  
17 the experiment.

18 The block copolymers of this invention can be represented by  
19 the following general formulae:



21 wherein each A is a polymer segment having an average molecular  
22 weight from about 100 to about 1,000,000 daltons chosen independently  
23 from homopolymers consisting of HDPE, homo and copolymers of cyclic  
24 olefins, such as polycyclopentene and polynorbornene, and isotactic,  
25 atactic, and syndiotactic poly-1-olefins such as atactic-PP,  
26 isotactic-PP, syndiotactic-PP; random copolymers of 1-olefins and  
27 diolefins such as ethylene-propylene rubber,  
28 ethylene-propylene-hexadiene rubber, ethylene-butene rubber, linear  
29 low density polyethylenes, such that no adjacent segments are the  
30 same polymer composition.

31 Novel block copolymers of this invention include but are not  
32 limited to diblock copolymers such as (HDPE)(EP), (i-PP)(EP),  
33 (LLDPE)(a-PP), (HDPE)(a-PP), (LLDPE)(HDPE) and the like, and triblock



- 31 -

1 copolymers such as (HDPE)(EP)(HDPE), (HDPE)(a-PP)(HDPE),  
 2 (HDPE)(EP)LLDPE), (LLDPE)(a-PP)(LLDPE), (HDPE)(a-PP)(LLDPE),  
 3 (i-PP)(EP)(i-PP), (s-PP)(EP)(s-PP) and the like. It will be recognized  
 4 to those well versed in the field that the isotactic polypropylene  
 5 segments contained in the block copolymers of this invention have  
 6 microstructure defects which are not observed in conventional i-PP  
 7 materials prepared using titanium Ziegler-Natta catalyst. The  
 8 microstructure defects which are unique to isotactic polypropylenes  
 9 prepared using metallocene catalysts arise from 1-3 and 2-1 additions to  
 10 propylene. The melting points of such materials can vary from 60°C to  
 11 165°C depending on the total number total defects.

12 The tapered copolymers can be represented by similar general  
 13 formula where the transitions between idealized polymer segments  $A_n$   
 14 are gradual. These gradient transitions between segments are  
 15 represented by arrows.

16  $(A_1) \text{---} \rightarrow (A_2) \text{---} \rightarrow (A_3) \text{---} \rightarrow \cdots (A_n).$

17 An example of this would be a polymer prepared by reacting a 50-50  
 18 mixture of ethylene and propylene with a living catalyst which has a  
 19 high preference for ethylene over propylene. The tapered polymer  
 20 obtained in such an experiment would be designated by the following  
 21 formula:

22 HDPE--->EP--->a-PP

- 32 -

EXAMPLES

1 Catalyst Preparation. The catalyst used in the following examples  
2 was prepared in dry, deoxygenated toluene (5.0 cc) by reacting  
3  $\text{Cp}_2\text{HfMe}_2$  with one equivalent of  $[\text{DMAH}][\text{B}(\text{pfp})_4]$  (where DMAH =  
4  $\text{PhMe}_2\text{NH}_4$  and pfp =  $\text{C}_6\text{F}_5$ ) at room temperature for 5-10 minutes. The  
5 reaction is known to cleanly produce methane gas and a single  
6 ionic catalyst  $[\text{Cp}_2\text{HfMe}(\text{PhNMe}_2)][\text{B}(\text{pfp})_4]$ .

Example 1First Ethylene then Propylene.

7 The reactor was cooled to  $0^\circ\text{C}$  and charged with 400 mls of  
8 toluene and 0.30 mmoles of catalyst. Ethylene (4.0 grams; 0.143  
9 moles) was added to the reactor. After all the ethylene was  
10 consumed, propylene (6 grams; 0.139 moles) was added; after 30  
11 minutes the reactor was dropped and the product collected. The  
12 crude product contained 50 mole % propylene, had an  
13  $M_n = 87,000$  with a molecular weight distribution of 3.0. The  
14 crude product was washed with hexane at room temperature to remove  
15 any -PP which was not in the form of block copolymer. The hexane  
16 insoluble material contained crystalline HDPE (as determined by  
17 IR) and 30 mole % propylene; the  $M_n$  was 144,000 with a molecular  
18 weight distribution of 1.89. The hexane soluble fraction was -  
19 PP, did not contain ethylene (by IR), and had an  $M_n$  of 63,000 with  
20 a molecular weight distribution of 1.47. Based on the extraction  
21 studies, it was concluded that 50-60% of the -PP chains were  
22 incorporated into a block copolymer under these conditions.

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1  $M_n = 87,000$  with a molecular weight distribution of 3.0. The crude  
2 product was washed with hexane at room temperature to remove any  
3  $\alpha$ -PP which was not in the form of block copolymer. The hexane  
4 insoluble material contained crystalline HDPE (as determined by IR)  
5 and 30 mole % propylene; the  $M_n$  was 144,000 with a molecular weight  
6 distribution of 1.89. The hexane soluble fraction was  $\alpha$ -PP, did  
7 not contain ethylene (by IR), and had a  $M_n$  of 63,000 with a  
8 molecular weight distribution of 1.47. Based on the extraction  
9 studies, it was concluded that 50-60% of the  $\alpha$ -PP chains were  
10 incorporated into a block copolymer under these conditions.

#### Example 2

##### First Propylene Then Ethylene

11 The procedure of Example 1 was repeated except propylene was  
12 added first. The crude product had 41 mole % propylene (IR), a  $M_n$   
13 of 170,000 with a molecular weight distribution of 1.78. A pad was  
14 pressed and extracted with hexane for 4 hours. At this point, the  
15 material contained 37 mole % propylene and very crystalline HDPE.  
16 The pad was further extracted with toluene at room temperature for 50  
17 hours with no loss of weight. The extracted "diblock" had a  $M_n$  of  
18 230,000 and a molecular weight distribution of 1.48 (the hexane  
19 solubles were  $\alpha$ -PP having a  $M_n$  of 125,000 and a molecular weight  
20 distribution of 1.72).

#### Example 3

##### Molecular Weight Control in Block Copolymer Synthesis

21 Using the procedure in Example 2, 3.0 grams of propylene  
22 (0.070 moles) were added to 0.30 mmole of the hafnium catalyst.  
23 After the propylene (0.071 moles) was completely consumed, 2.0 grams  
24 of ethylene were added to the system. The resulting product was  
25 washed with hexane at room temperature to remove any  $\alpha$ -PP. The  
26 resulting block copolymer had a  $M_n$  of 107,000 and a molecular weight  
27 distribution of 1.68, and contained 42 mole % propylene by IR  
28 spectroscopy.

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Example 4Effect of Temperature

1           If the temperature is raised the effect is to lower the  
2 efficiency of the block formation. The temperature was raised from  
3 0°C to 10°C and the blocking efficiency was reduced to less than 10%  
4 to 65%. When the temperature was lowered to -5°C, the blocking  
5 efficiency improved 78%.

Example 5

The Effect of Increasing the Time  
Between the Addition of Monomers

6           A series of block copolymerizations were run at 0°C and the  
7 time between the addition of propylene and ethylene was varied from 6  
8 to 42 minutes. The crude products were collected, analyzed by GPC  
9 and IR, then extracted with hexane at room temperature for 65 hours  
10 to remove unblocked  $\alpha$ -PP. In a well-behaved system wherein the  
11 extraction technique removes all of the  $\alpha$ -PP, a logarithmically  
12 increase in the percent of hexane extractables with time would be  
13 expected. The data of this example is shown in Fig. 1 in graphical  
14 form. The Y-axis represents the percent of polypropylene which is  
15 incorporated into the block copolymer. The extractables were  
16 isolated and analyzed by GPC and IR; they were all pure  $\alpha$ -PP. . The  
17 correlation is close to the linear result expected so that this  
18 technique can be used to evaluate the kinetics of chain loss under a  
19 variety of conditions. This result confirms the ability to make true  
20 block copolymers, and confirms that hexane extraction is a good  
21 measure of block copolymer efficiency for this polymer system.

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Example 6Preparation of EP

1 In this example, 1.6 grams of propylene (0.037 moles) were  
2 added to  $[\text{Cp}_2\text{HfMe}(\text{L})][\text{B}(\text{pfp})_4]$  (0.30 mmole) in 400 cc of  
3 toluene at 0°C. Immediately after the propylene addition, 1.1 grams  
4 of ethylene (0.039 moles) was metered in over 3 minutes. After six  
5 minutes, the product was recovered yielding 2.7 grams of amorphous EP  
6 rubber. The product was non-crystalline by IR; the polymer had a  
7  $M_n$  of 96,000 and a molecular weight distribution of 1.69.

Example 7Preparation of EP

8 In this example, 3.2 grams of propylene (0.074 moles) was  
9 added to  $[\text{Cp}_2\text{HfMe}(\text{L})][\text{B}(\text{pfp})_4]$  (0.30 mmole) in 400 cc of  
10 toluene at 0°C. Ethylene (2.2 grams; 0.078 moles) was added to the  
11 reactor over 5.5 minutes. The product was recovered yielding 5.7  
12 grams of EP rubber having a  $M_n$  of 155,000, and a molecular weight  
13 distribution of 1.48. The IR showed some degree of PE-crystallinity.

Example 8Preparation of EP-b-HDPE

14 Example 6 was repeated to prepare "living" EP-rubber. After  
15 all the monomer had been consumed, ethylene (1.1 grams) was added to  
16 prepare the desired block copolymer. The product was recovered  
17 yielding 4.25 grams of copolymer. The IR showed PE crystallinity and  
18 the polymer had thermoplastic-like properties. The onset of  $T_g$  was  
19 -52.9°C and the product had a melting point of 119°C. The  $M_n$  of  
20 the crude product was 161,000 with a molecular weight distribution of  
21 1.59.

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1    Example 9.    The intention of this example is to demonstrate  
2    that slow chain transfer can be used to catalytically prepare  
3    block copolymers. This is an example of in-situ catalyst  
4    recycle leading to the production of mixtures of small  
5    amounts of homopolymer and mixtures of multiblock copolymers  
6    (AB, ABA, BAB etc).

7    The reactor was cooled to 0°C and charged with 400 mls of  
8    toluene and 0.15 mmole of catalyst. In step 1, propylene  
9    (1.5 grams) was added to the well stirred reactor causing a  
11   pressure increase of 7 psi. After 7 minutes the pressure in  
12   the reactor dropped to zero and the reactor was vented  
13   through a nujol bubbler to remove any residual propylene in  
14   the system. In step 2, ethylene (1.0 grams) was added. The  
15   ethylene was consumed in less than one minute. After all the  
16   ethylene was consumed the reactor was vented. These  
17   sequential steps were repeated 5 more times resulting in  
18   similar monomer conversion rates. The reactor was dropped  
19   and the the product was collected yielding 15 grams after  
20   drying. The crude product was analyzed by GPC and had a Mn =  
21   122K and a MWD = 2.2. The melting point was 126°C by DSC and  
22   the IR indicated the presence of high crystallinity  
23   polyethylene. A thin pad weighing 1.25 grams was compression  
24   molded and extracted with hexane a room temperature for 72  
25   hours at room temperature. The pad was removed, dried and  
26   weighed yielding 1.13 grams of insoluble material. The  
27   insoluble material was analyzed by GPC and DSC and had a Mn =  
28   171K, a MWD = 1.8 and a melting point of 126°C. The soluble  
29   material was isolated (0.12 grams) and was identified as  
30   atactic PP. The extraction data indicated that 84% of the  
31   polypropylene is bonded to insoluble polyethylene segments.  
32   The data are not sufficient to detect homo-polyethylene, or  
33   to quantify the ratios of the various possible multiblock  
34   copolymers. The observation, however, that the Mn of the  
35   crude and extracted products in this experiment are only  
36   slightly higher than is typical of a standard A-B sequential  
37   addition (Mn = 1201-140K) at the same monomer:catalyst ratio  
39   suggests that the chain lifetimes are not sufficiently long  
40   to produce high amounts of triblock or other higher order  
41   block copolymers.

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1    Example 10.    The reactor was cooled to 0°C and charged with  
2    400 mls of toluene and 0.15 mmole of catalyst. In step 1,  
3    propylene (1.5 grams) was added to the well stirred reactor  
4    causing a pressure increase of 7 psi. After 7 minutes the  
5    pressure in the reactor dropped to zero and the reactor was  
6    vented through a nujol bubbler to remove any residual  
7    propylene in the system. In step 2, ethylene (1.0 grams) was  
8    added. The ethylene was consumed in less than one minute.  
9    After all the ethylene was consumed the reactor was vented  
10   and in step 3 propylene (1.5 grams) was added. The propylene  
11   was consumed in 7 minutes and after an addition 20 minute  
12   waiting period steps 1,2 and 3 were repeated. The reactor  
13   was dropped and 4 grams of crude dry product was isolated.  
14   The crude product was analyzed by GPC and had a Mn = 140K and  
15   a MWD = 1.7. The IR spectrum indicated the presence of high  
16   crystallinity polyethylene. A thin pad weighing 1.07 grams  
17   was compression molded and extracted with hexane a room  
18   temperature for 72 hours at room temperature. The pad was  
19   removed, dried and weighed yielding 0.87 grams of insoluble  
20   material. The insoluble material was analyzed by GPC had a  
21   Mn = 192K, a MWD = 1.4. The soluble material was isolated  
22   (0.20 grams) and was identified as atactic PP by IR and NMR  
23   spectroscopy. The extraction data indicated that 81% of the  
24   polypropylene is bonded to insoluble polyethylene segments.

25   Example 11.    In this example we describe an attempt to  
26   prepare an ABA triblock copolymer where the A-block is high  
27   density polyethylene and the B-block is elastomeric atactic  
28   polypropylene. We disclose a technique where a small amount  
29   of propylene (5% of the amount added in the B-step) is added  
30   in a prepolymerization step. The effect of this is to  
31   solubilize the insoluble polyethylene A-segment and prevent  
32   precipitation of the living polymer. When this procedure is  
33   used a clear, apparently homogeneous reaction mixture is  
34   formed. Similar experiments where the prepolymerization step  
35   is not used gives a heterogeneous reaction mixture, lower  
36   blocking efficiencies and broader molecular weight  
37   distributions.

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1       The reactor was cooled to 0°C and charged with 400 mls of  
2       toluene and 0.15 mmole of catalyst. In a prepolymerization  
3       step 1, propylene (0.15 grams) was added to the well stirred  
4       reactor. After 7 minutes the pressure in the reactor dropped  
5       to zero and the reactor was vented through a nujol bubbler to  
6       remove any residual propylene in the system. In step 2,  
7       ethylene (0.5 grams) was added. After 2 minutes, propylene  
8       (3.0 grams) was added to the well stirred reactor causing a  
9       pressure increase of 7 psi. The propylene was consumed in 4  
10      minutes at which point the reactor was vented and ethylene  
11      (0.5 grams) was added. The reactor was dropped and  
12      approximately 4 grams of crude dry product was isolated. The  
13      crude product was analyzed by GPC and DSC and had a melting  
14      point of 122°C, a Mn = 173K and a MWD = 1.9 (with a bimodal  
15      shape). A thin pad weighing 1.295 grams was compression  
16      molded and extracted with hexane a room temperature for 72  
17      hours at room temperature. The pad was removed, dried and  
18      weighed yielding 1.17 grams of insoluble material. The  
19      resulting material has thermoplastic elastomeric properties.  
20      The extraction data indicated that 86% of the polypropylene  
21      is bonded to insoluble polyethylene segments.

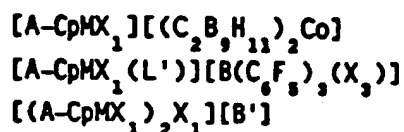
22      Example 12. The reactor was cooled to 0°C and charged with  
23      400 mls of toluene and 0.15 mmole of catalyst. In a  
24      prepolymerization step 1, propylene (0.15 grams) was added to  
25      the well stirred reactor. After 7 minutes the pressure in  
26      the reactor dropped to zero and the reactor was vented  
27      through a nujol bubbler to remove any residual propylene in  
28      the system. In step 2, ethylene (0.25 grams) was added.  
29      After 2 minutes, propylene (3.0 grams) was added to the well  
30      stirred reactor causing a pressure increase of 7 psi. The  
31      propylene was consumed in 4 minutes at which point the  
32      reactor was vented and ethylene (0.25 grams) was added. The  
33      reactor was dropped and approximately 3.5 grams of crude dry  
34      product was isolated. The crude product was analyzed by GPC  
35      and DSC and had a melting point of 122°C, a Mn = 160K and a  
36      MWD = 1.8 (with a bimodal shape). A thin pad weighing 1.288  
37      grams was compression molded and extracted with hexane a room  
38      temperature for 72 hours at room temperature. The extremely  
39      swollen pad was removed, dried and weighed yielding 1.165  
40      grams of insoluble material. The resulting material has  
41      thermoplastic elastomeric properties. The extraction data  
42      indicated that 88% of the polypropylene is bonded to  
43      insoluble polyethylene segments. The insoluble product was  
44      analyzed by GPC and had a Mn = 184K and a MWD = 1.6 (with a  
45      bimodal shape).



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CLAIMS

1. A process for the production of block copolymers comprising:
  - (i) contacting a first olefinic monomer(s) with a catalyst which is the reaction product of:
    - (a) a metallocene component, and
    - (b) a second component having a cation capable of donating a proton and a compatible non-coordinating anion to produce a first living polymer; and
  - (ii) sequentially adding to said living polymer at least a second monomer(s) to copolymerize with said first polymer to produce a multi block copolymer; and
  - (iii) recovering a block copolymer
2. The process of claim 1 wherein the block copolymer is a diblock copolymer.
3. The process of claim 1 wherein the block copolymer is a triblock.
4. The process of claim 1 wherein the catalyst reaction product is of the formulae:



wherein: M is titanium, zirconium or hafnium; (A-Cp) is either (Cp)(Cp\*) or Cp-A'-Cp\* and Cp and Cp\* are the same or different substituted or unsubstituted cyclopentadienyl radicals; A' is a covalent bridging group containing a Group IV-A element; L' is a neutral Lewis base; X<sub>1</sub> is a hydride radical, hydrocarbyl radical having from 1 to about 20 carbon atoms, substituted-hydrocarbyl radical, wherein 1 or more of the hydrogen atoms are replaced with a

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halogen atom, having from 1 to about 20 carbon atoms, or organo-metalloid radical comprising a Group IV-A element wherein each of the hydrocarbyl substituents contained in the organo portion of said organo-metalloid, independently, contain from 1 to about 20 carbon atoms;  $C_1-C_{20}$  and  $X_3$  is a hydride, halide, hydrocarbyl radical, a  $C_1-C_{20}$  hydrocarbyl radical wherein one or more of the hydrogen atoms is replaced by a halogen atom, organometalloid radical wherein each hydrocarbyl substitution in the organo portion contains from 1 to 20 carbon atoms and the metal is a Group IVA metal.

5. The process of claim 4 wherein the catalyst reaction product is represented by the formula:

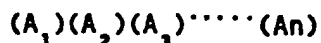


6. The process claim 1, wherein the catalyst is the reaction product bis(cyclopentadienyl) hafnium dimethyl and N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron.

7. The process of claim 1 wherein said steps of reacting, copolymerizing, introducing and repeating are carried out at a temperature of from about  $-5^{\circ}C$  to about  $10^{\circ}C$ .

8. The process of claim 1 wherein any of said monomers is selected from ethylene, propylene, 1-butene.

9. Olefinic block copolymers having a Mw/Mn of from about 1 to 5 represented by the formula:



wherein each A represent a polymer segment having an average of Mw of from 100 to about 1,000,000 daltons, each adjacent A represents a different olefinic polymer segment, A being selected from HDPE, atactic-1-olefins, isotactic 1-olefins, syndiotactic 1-olefins, homo-

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and copolymers of cyclic olefins, and random copolymers of 1-olefins and diolefins.

10. The olefin block copolymers of claim 9 wherein the polymer segments are selected from atactic-polypropylene, isotactic-polypropylene and syndiotactic-polypropylene.

11. Olefin block copolymers of claim 11 wherein said block copolymers is a diblock.

12. Olefin block copolymers of claim 11 selected from (HDPE)(EP), (i-PP)(EP), (LLDPE)(a-PP), (LLDPE)(HDPE).

13. Olefin block copolymers of claim 10 wherein said block copolymer is a triblock.

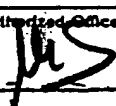
14. Olefin block copolymers of claim 13 selected from (HDPE)(EP)(HDPE), (HDPE)(EP)(LLDPE), (LLDPE)(a-PP)(LLDPE)(HDPE)(a-pp)(LLDPE), (i-PP)(EP)(i-PP)(s-pp)(EP)(s-PP).

15. Mixtures of homopolyolefins, and di- and triblock copolymers, said block copolymers produced by the process of claims 2 and 3.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/00835

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>5</sup> : C 08 F 297/08, C 08 F 4/64		
<b>II. FIELDS SEARCHED</b> Minimum Documentation Searched		
Classification System	Classification Symbols	
IPC <sup>5</sup>	C 08 F 4/00, C 08 F 293/00, C 08 F 297/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages **	Relevant to Claim No. **
A	DE, A1, 3 826 075 (HOECHST AG) 01 February 1990 (01.02.90), see claims 1-6, 9; examples.	1-4, 7- 11, 13, 15
A	DE, A1, 3 640 924 (HOECHST AG) 01 June 1988 (01.06.88), see claims 1-4; examples.	1-4, 7- 11, 13
A	US, A, 4 522 982 (EWEN) 11 June 1985 (11.06.85), see claims 1, 6, 8; examples.	1, 4, 7- 10, 15
A	US, A, 4 408 019 (BLUNT) 04 October 1983 (04.10.83), see claim 1; examples (cited in the application).	1, 3, 4, 7-9
A	EP, A1, 0 277 004	1, 4-6
* Special categories of cited documents: ** -A- document defining the general state of the art which is not considered to be of particular relevance -E- earlier document but published on or after the international filing date -L- document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) -O- document referring to an oral disclosure, use, exhibition or other means -P- document published prior to the international filing date but later than the priority date claimed -T- later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention -X- document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step -Y- document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art -Z- document member of the same patent family		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search 19 April 1991		Date of Mailing of this International Search Report 24. 05. 91
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer  M. SOTELO

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	(EXXON CHEMICAL PATENTS INC.) 03 August 1988 (03.08.88), see claims 1-4,6,7. --- EP, A1, 0 277 003 (EXXON CHEMICAL PATENTS INC.) 03 August 1988 (03.08.88), see claims 1-3,13. -----	1,4